

Supporting Information

Discovery of Fluidic LiBH_4 on Scaffold Surfaces and its Application for Fast Co-Confinement of $\text{LiBH}_4\text{-Ca}(\text{BH}_4)_2$ into Mesopores

Hyun-Sook Lee,[†] Son-Jong Hwang,^{‡} Magnus To,[‡] Young-Su Lee,^{*†} and Young Whan Cho[†]*

[†]High Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

[‡]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

***Corresponding authors:** Son-Jong Hwang E-mail: sonjong@cheme.caltech.edu Tel: +1-626-395-2323; Young-Su Lee E-mail: lee0su@kist.re.kr Tel: +82-2-958-5412.

Supporting Information: The structural characterization of the synthesized SBA-15 was performed. The inset of Figure S1(a) presents Type IV adsorption/desorption isotherm meaning mesoporous products with channel-type pores. The pore size distribution analyzed by Barrett-Joyner-Halenda (BJH) method shown in the inset of Figure S1(a) indicates that the SBA-15 has a pore diameter of ~6.4 nm. Small angle X-ray diffraction (XRD) patterns in Figure S1(b) show clearly the (100), (110), and (200) reflections associated with the two-dimensional hexagonal symmetry ($p6mm$) of SBA-15. The results of N₂ physisorption and small angle XRD depict the successful synthesis of well-ordered periodic mesopore structured SBA-15. The structural parameters are summarized in Table S1.

Table S1. Structural properties of SBA-15.

| D _{BJH} (nm) ^a | d ₁₀₀ (nm) ^b | a ₀ (nm) ^c | W (nm) ^d | S _{BET} (m ² g ⁻¹) | V _{meso} (cm ³ g ⁻¹) | V _{micro} (cm ³ g ⁻¹) | V _{total} (cm ³ g ⁻¹) |
|------------------------------------|------------------------------------|----------------------------------|---------------------|--|---|--|--|
| 6.3 | 9.70 | 11.20 | 4.90 | 677.0 | 0.61 | 0.16 | 0.73 |

^aD_{BJH} is the maximum value of the BJH pore size distribution peak deduced from the adsorption branch of the N₂ isotherm. ^bd₁₀₀ is the XRD (100) interplanar spacing. ^ca₀ is the unit cell parameter ($a_0 = 2 \times (d_{100}/\sqrt{3})$). ^dW is the pore wall thickness ($W=a_0-D_{BJH}$).

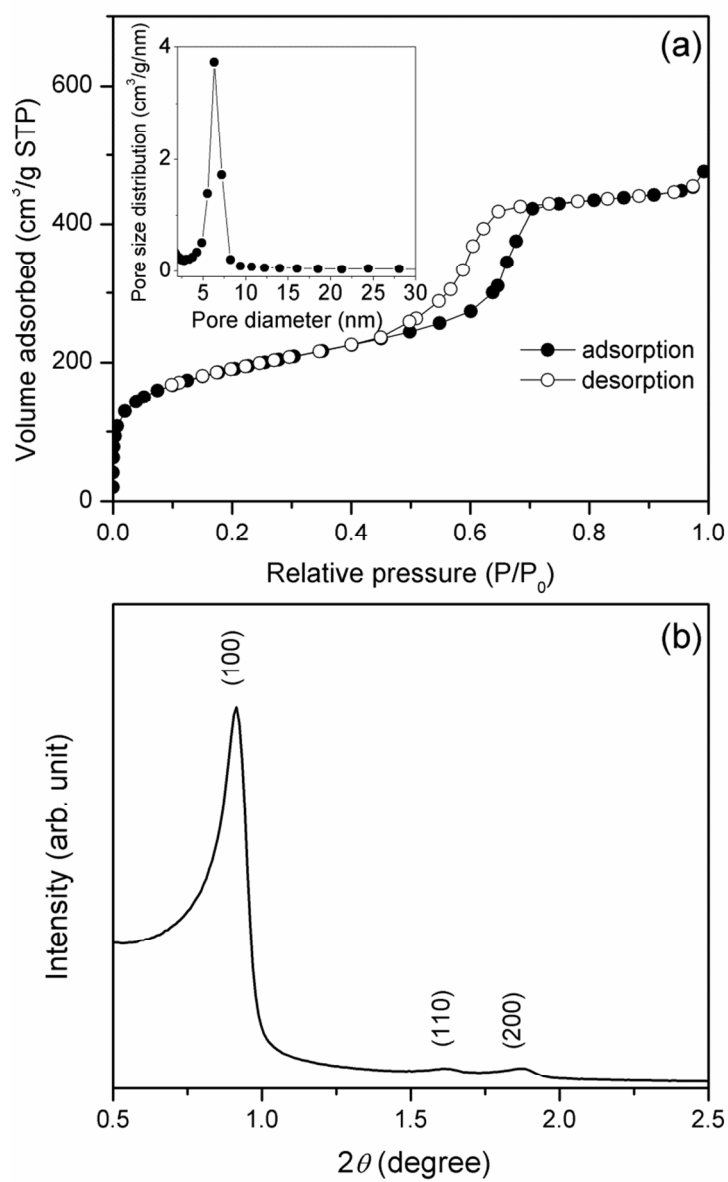


Figure S1. (a) N_2 adsorption and desorption isotherms (inset: Pore size distribution) and (b) X-ray diffraction patterns at small angles for the SBA-15 with 6.3 nm of pore size.

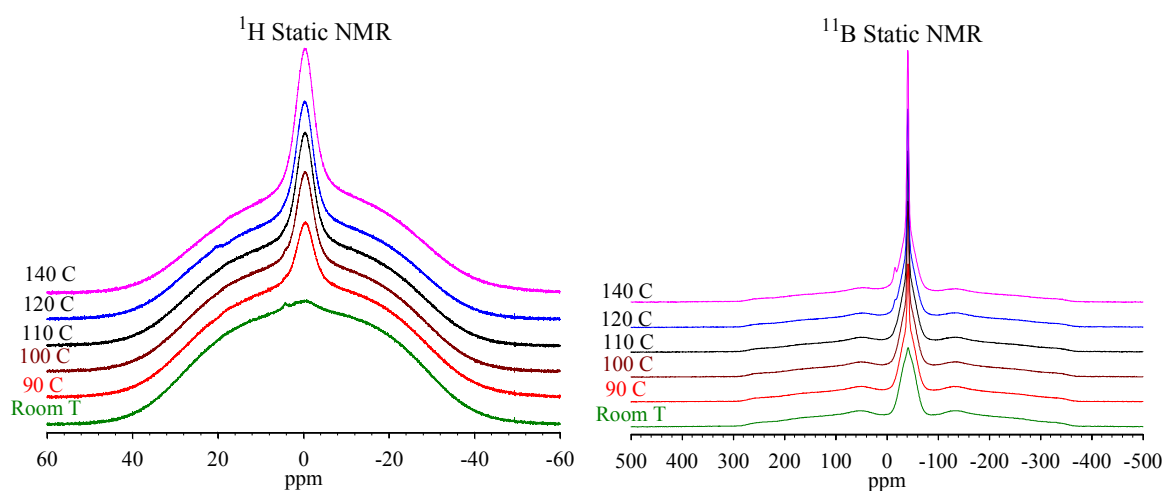


Figure S2. ^1H and ^{11}B static NMR spectra of HM-LB/MCM-41 sample recorded at room temperature after heating for 5 hours in a furnace at temperatures listed in spectra. The quadrupole echo sequence was used to recover ^{11}B NMR powder pattern.

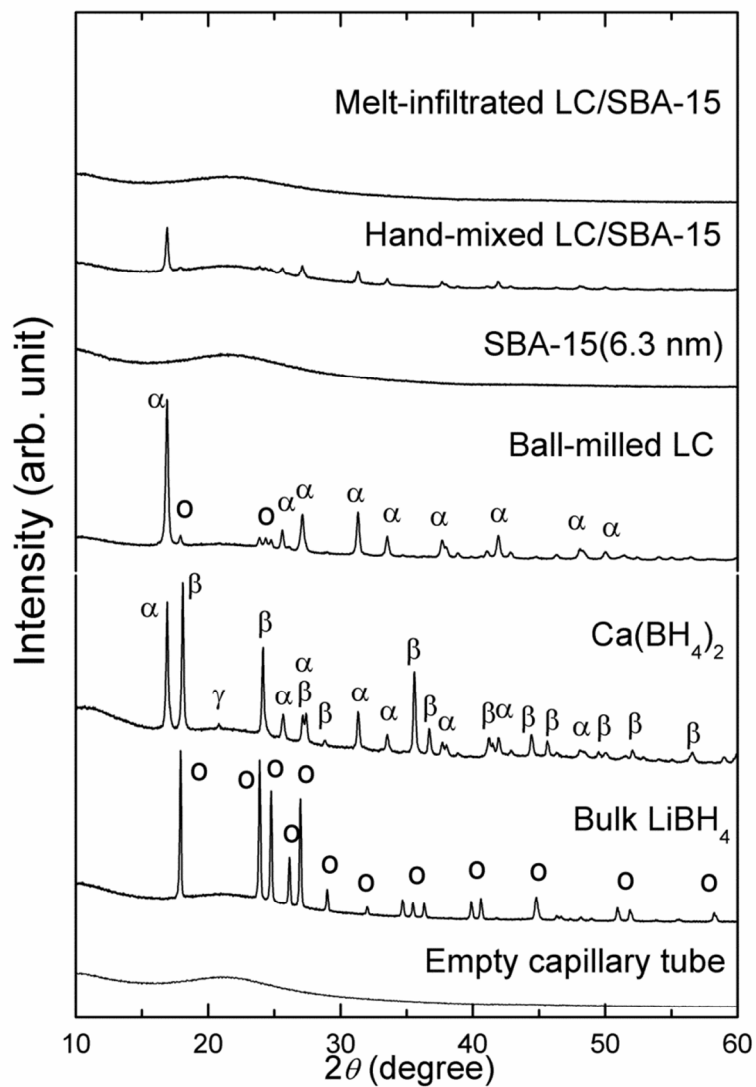


Figure S3. XRD patterns of LiBH_4 and $\text{Ca}(\text{BH}_4)_2$ in bulk phases, ball milled LC, SBA-15, HM-LC/SBA-15, MI-LC/SBA-15 samples (see Table S1 and text). LC $\equiv 0.68\text{LiBH}_4 + 0.32\text{Ca}(\text{BH}_4)_2$, an eutectic composition.

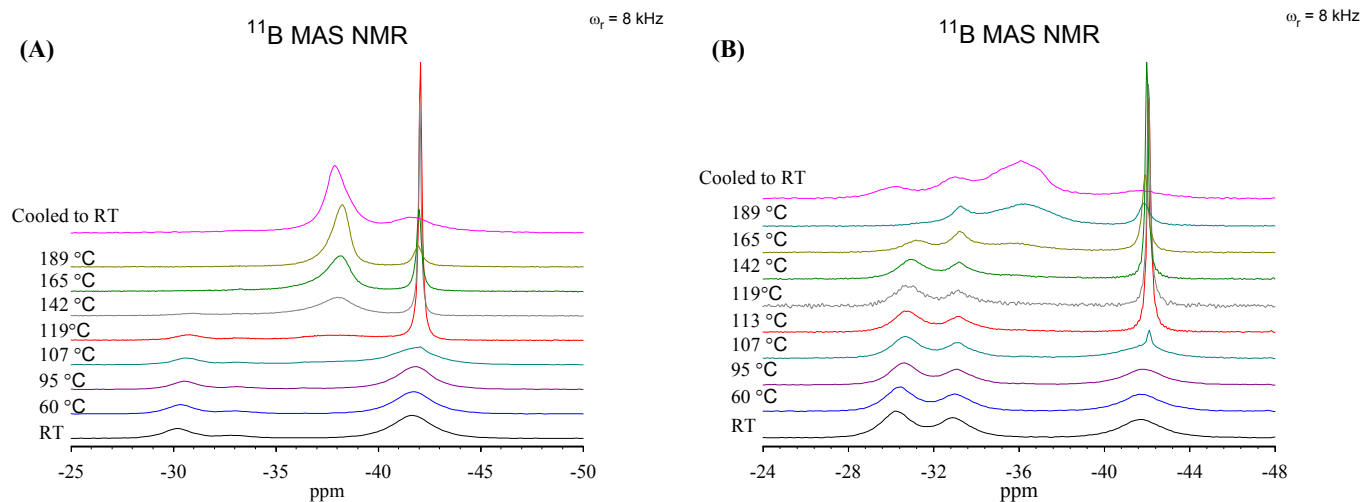


Figure S4. ^{11}B stack plots from *in situ* VT NMR experiments on HM-LC/MCM-41 for non-eutectic compositions of LC ($x\text{LiBH}_4 - y\text{Ca}(\text{BH}_4)_2$) mixtures. (A) $x:y=4:1$ mole ratio with LiBH_4 being dominant in mixed bulk powder, (B) $x:y=1:1$.

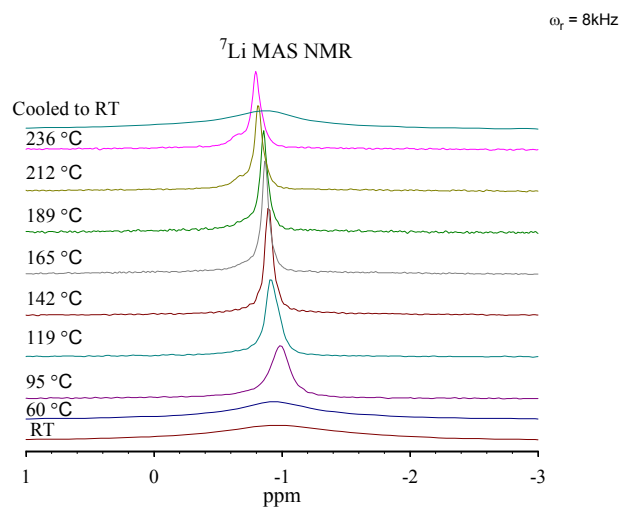


Figure S5. ${}^7\text{Li}$ MAS NMR spectra at various temperatures of the MI-LC/SBA-15 sample.

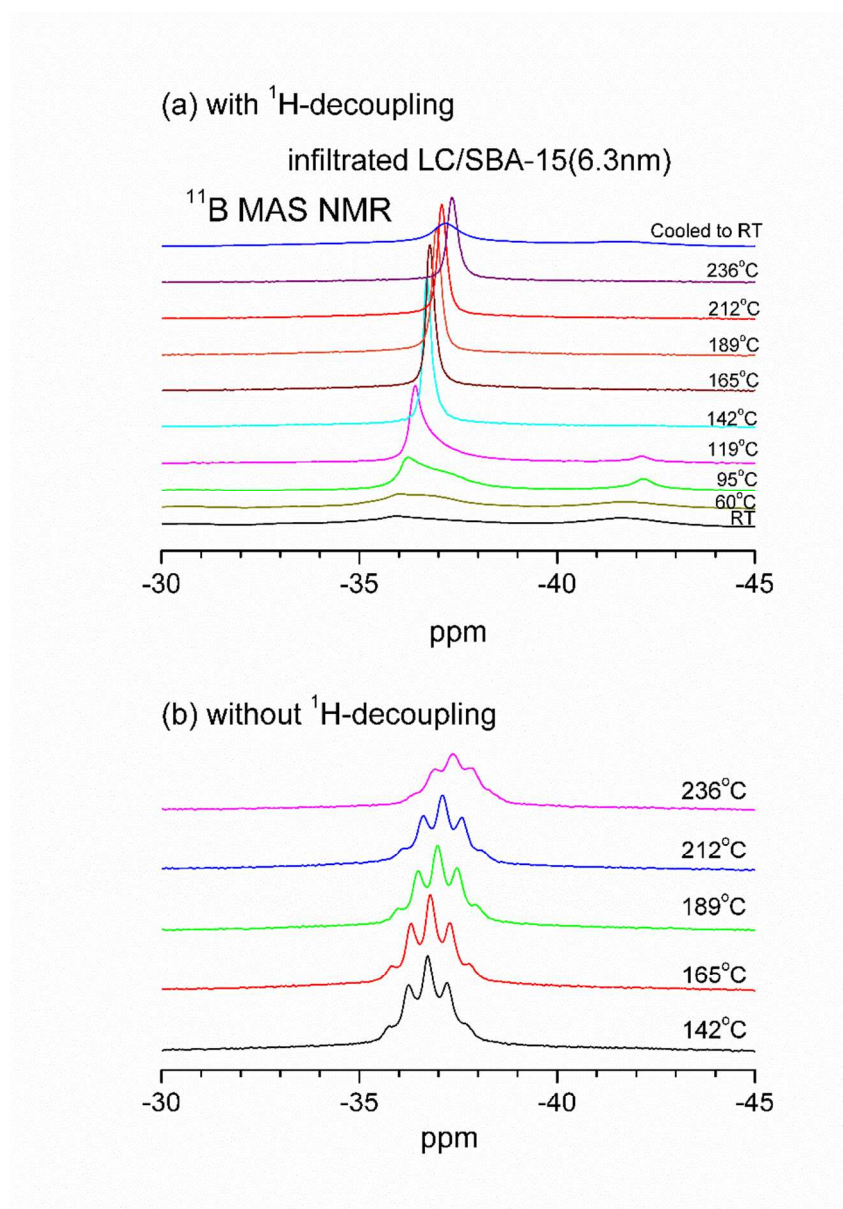


Figure S6. *In situ* ^{11}B VT MAS NMR spectra of the MI-LC/SBA-15 sample, which was measured (a) with and (b) without ^1H -decoupling. The melt-infiltration of the sample was performed by heating at 230 °C for 30 min under $p(\text{H}_2) = 100$ bar. Clear splitting patterns of ^{11}B – ^1H J -coupling are observed for the nanoconfined mixed-phase at the temperature above ~120 °C when proton decoupling is applied.

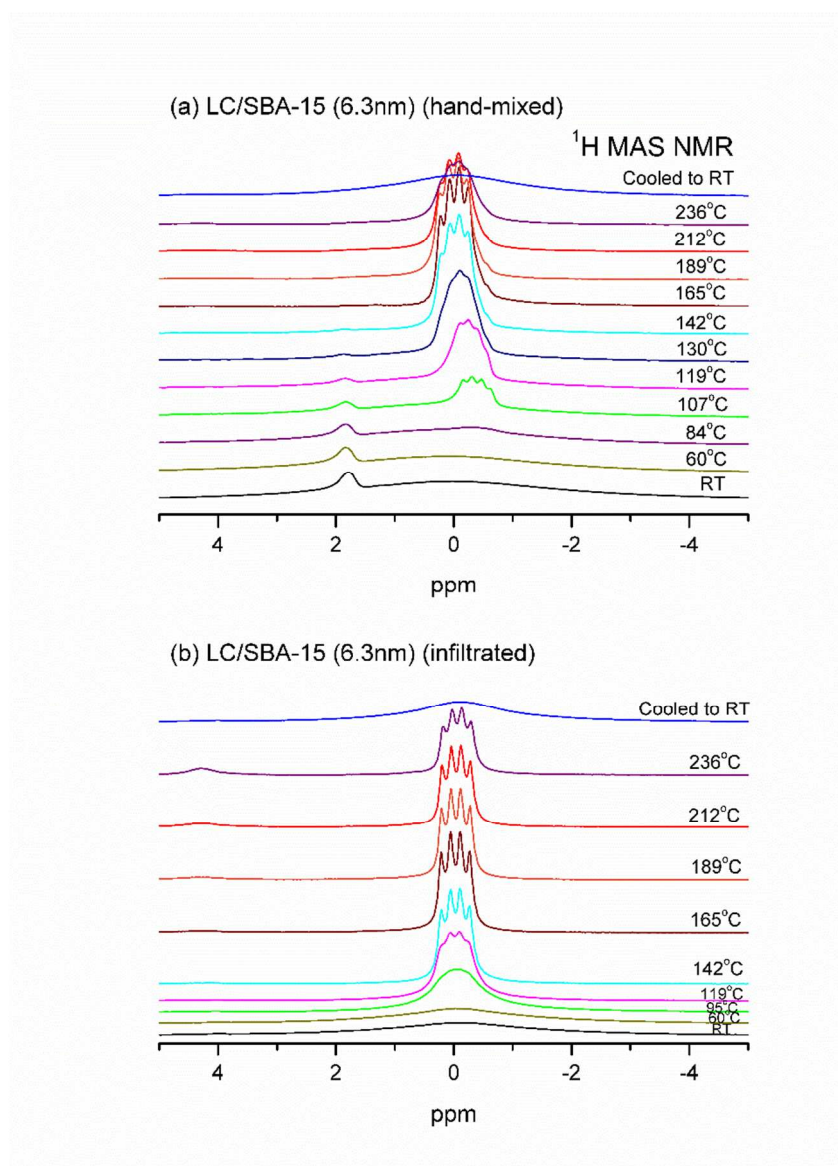


Figure S7. *In situ* ¹H VT MAS NMR spectra of (a) HM-LC/SBA-15 and (b) MI-LC/SBA-15 samples.